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# Surface studies of fly ash zeolites via adsorption/desorption isotherms

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Zeolites of types Na-A (Linde, LTA) and Na-X (Faujasite, FAU) are perspective adsorbents in environment protection systems due to their extremely developed surface area and pore size exceeding molecular diameter of variety gaseous pollutants. Recently, synthetic analogous of these zeolites being obtained of aluminosilicate residues for saving natural resources. In this study LTA and FAU zeolites were synthesized by alkaline conversion of coal fly ash by different techniques in order to be further applied for adsorption of carbon dioxide from flue gases. The main key factors predeterminating the adsorption ability of solids are their surface and porosity characteristics. For these considerations, selected samples were subjected to surface studies by the help of surface area and porosity analyzer Tristar II 3020, Micromeritics. Experimental adsorption/desorption isotherms were measured at 77 K using analytical gas nitrogen 5N. Specific surface areas ($S_{BET}$, $m^2/g$) of the investigated samples were evaluated applying the standart multi-point Brunauer-Emett-Teller (BET) model to the adsorption data. The raw fly ash is characterized with a very low specific surface area of 10 $m^2/g$, while $S_{BET}$ values for the fly ash zeolites (FAZ) of Na-X type were found in the range of 125-250 $m^2/g$ depending on the synthesis procedures applied. The highest specific BET surface area of 280 $m^2/g$ in the frame of this study was measured for FAU type coal fly ash zeolite, obtained by atmospheric self-crystallization for about of a year. However, FAZ possess three times lower $S_{BET}$ values in comparison to a referent zeolite Na-X prepared from pure components. Mesopore distribution was studied by the Barrett-Joyner-Halenda (BJH) model applied to the experimental desorption isotherms. Micropore volume/area yield was computed from the adsorption data using t-plot model.

**Key words:** fly ash zeolites, surface area, porosity, adsorption isotherms

## INTRODUCTION

Since tens of years, enormous amounts of ash residues including bottom ash, boiler slag and fly ash (FA) are generated all over the world by coal supplied Thermal Power Plants (TPP). Recently, different approaches for high-value added utilization of coal ash in practice have been developed instead of its disposal in landfills [1,2]. Thus, this solid by-product became a raw material for production of building materials, composites, agricultural amendments, geopolymers, low-cost adsorbents, as well as a source for separation of ferrous oxides (magnetite, hematite) or for extraction of titanium oxide, alumina, cenospheres, etc. Due to aluminosilicate macro composition of FA, its conversion into zeolites has been widely investigated [3,4]. Fly ash zeolites (FAZ) similarly to their natural and pure synthetic analogies are perspective materials for many advanced applications such as ion-exchangers, molecular sieves, and adsorbents [5,6]. Making efforts for finding a solution of global warming by reduction of the greenhouse gas emissions exhausted into the atmosphere, zeolites have been studying as potential adsorbents for carbon dioxide uptake from flue gas streams. Physical adsorption of $CO_2$ on solids possesses a number of advantages in comparison to the broadly studied chemisorption by amine-based solutions consisting of technical feasibility, low-energy desorption, environmental harmless, process reversibility, absence of secondary liquids, adsorbent multiple usage without loses, and cost effectiveness [7]. Pressure (PSA) and vacuum swing adsorption (VSA) have been considered as the main potential techniques for capture of $CO_2$ from flue gas flows [8,9]. Many studies on carbon dioxide sequestration on commercial 5A (CaA) and 13X (NaX) zeolites have been done indicating their high capacity and preferential adsorption toward $CO_2$ [10,11]. FAZ have to meet a numbers of requirements mostly directed to their surface properties for being competitive in practice. The most recently, the research interest has been provoked by the FAZ suitability as adsorbents of carbon dioxide in post-combustion carbon capture systems striving to develop zero emission TPP [12]. However, the implementation of such innovative technology claims materials with extremely developed specific surface area and appropriate pore size distribution.

This study is focused on the evaluation of the main surface characteristics of fly ash zeolites of

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Na-X (Faujasite, FAU) and Na-A (Linde, LTA) types by experimental adsoption and desorption isotherms in comparison to those of the raw fly ash and pure synthetic zeolite Na-X as a referent.

## EXPERIMENTAL

FAZ were synthesized by alkaline conversion of lignite coal fly ash collected by the electrostatic precipitators of TPP "Maritza East 2" in Bulgaria. Chemical and phase composition, morphology and the main thermal properties of the raw FA were previously studied [13]. Zeolite phases were obtained by three manners of alkaline activation of FA, as follows: (1) double stage fusion-hydrothermal synthesis; (2) self-crystallization of FA/sodium hydroxide mixtures at room conditions; (3) hybrid fusion/self-crystallization method. The influence of the synthesis conditions on the morphology, phase composition and crystallinity of the obtained zeolites was investigated [14,15].

Nitrogen adsorption/desorption isotherms of selected FAZ samples, raw FA and a referent Na-X obtained from pure starting components were measured at 77 K using a volumetric adsorption analyzer Tristar II 3020, Micromeritics. Samples were preliminary degassed in a set-up FlowPrep 60, Micromeritics, at 260 °C for 2 h under helium flow. BET specific surface areas ($S_{BET}$, $m^2/g$) were evaluated applying the multi-point Brunauer–Emmett–Teller (BET) model for description of the experimental nitrogen adsorption data in the range of relative pressures $p/p_0$ corresponding to formation of monolayer. Mesopore distribution for the investigated FAZ, FA and the referent zeolite Na-X (FAU) was studied from the desorption branch of the isotherms by the Barrett-Joyner-Halenda (BJH) model. The theory of the models can be found in Ref. [16]. Micropore volume/area yield was evaluated using t-plot model for the adsorption data.

## RESULTS AND DISCUSSION

### *Preliminary studies*

The raw FA used for these studies is mostly aluminosilicate material consisting of $SiO_2$ and $Al_2O_3$ in a ratio of 2.25, as their total amount exceeds 76 wt. %. The amorphous vs. crystalline part was found to be 43/57. FA was used as a starting material for synthesis of zeolites by alkaline activation with sodium hydroxide (NaOH) applying three different methods for preparation, designated as follows: (1) atmospheric self-crystallization; (2) two stage fusion-hydrothermal synthesis and (3) two-stage fusion-atmospheric crystallization. Synthesis conditions of the investigated samples are summarized in Table 1, while more detailed description can be found in Refs. [15,17]. The obtained FAZ were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM) to identify their phase composition and morphology. The predominant zeolite phase obtained at different synthesis conditions is indicated in Table 1.

### *$N_2$-adsorption/desorption isotherms*

The experimental $N_2$-adsorption/desorption isotherms of the investigated FAZ, starting FA and referent Na-X zeolite are plotted in Fig.1. The isotherms represent the function between the amount of the adsorbed gas (mmol) by unit mass of solid (g) and the relative pressure $p/p_0$, which is the ratio between the equilibrium (p) and the saturation pressure ($p_0$) at T=77 K.

The types of the isotherms were described according to the IUPAC classification (1985). A thorough analysis of the shapes of different physisorption isotherms in view of material structure has been made in Ref. [18]. FA shows a $N_2$-adsorption isotherm of type II that is usually typical for non-porous or macroporous materials with relatively small specific surface area (Fig. 1).

An adsorption-desorption hysteresis loop of H3 shape, which is normally attributed to materials

**Table 1**. Synthesis conditions of FAZ samples.

| Sample | Method of FAZ synthesis | FA/NaOH ratio | NaOH M | Fusion at 90 ºC for 1 hour | Synthesis temperature, ºC | Time of synthesis | FAZ type |
|---|---|---|---|---|---|---|---|
| **A-2** | Atmospheric self-crystallization | 1/0.6 | 1.5 | NO | approx. 20 | 240 days | X |
| **A-3** | Atmospheric self-crystallization | 1/0.6 | 1.5 | NO | approx. 20 | 360 days | X |
| **FH-5** | Two stage fusion-hydrothermal | 1/1.6 | 2 | YES | 90 | 4 hours | A |
| **FH-7** | Two stage fusion-hydrothermal | 1/2.4 | 3 | YES | 90 | 4 hours | X |
| **FA-1** | Two stage fusion-atmospheric | 1/1 | 2.5 | YES | approx. 20 | 30 days | X |

containing slit-shaped pores can be observed. Physical sorption isotherms of type II have also been reported for F-class FA in other investigations [19]. The referent Na-X sample exhibits adsoption isotherm of type I with a narrow desorption loop most similar to H4 shape. The adsorption of $N_2$ on the Na-X zeolite rises rapidly at low relative pressures $p/p_0<0.01$ filling almost the entire free volume available, and thereafter the adsorbed quantity increases slowly attaining a nearly horizontal plateau. This is indicative for size-distribution of micropores in a limited range and for a very small external surface area. Hysteresis loops of type H4 are also given by slit-shaped pores, but in this case the pore size distribution is mainly in a microscale range. Taking into account the narrow area of adsoption/desoption loop, it can be assumed that the FAU used as a referent sample is a microporous material consisting predominantly of cylindrical pores with a defined pore width, and a small yield of slit-shaped pores. At $p/p_0>0.95$, the isotherm of Na-X begins to increase indicating the presence of some macropores [18]. FAZ FH-5 which is predominantly composed of zeolite A crystalline phase characterizes with an isotherm of type II that is very similar in shape to those of the raw FA. However, some differences can be observed between the two isotherms that can be summarized as follows: at FAZ FH-5 the hysteresis loop is narrower and the adsorption and desorption branches coincide at $p/p_o$ below 0.4, while at FA a very small deviation between the branches can be observed resulting in an opened isotherm.

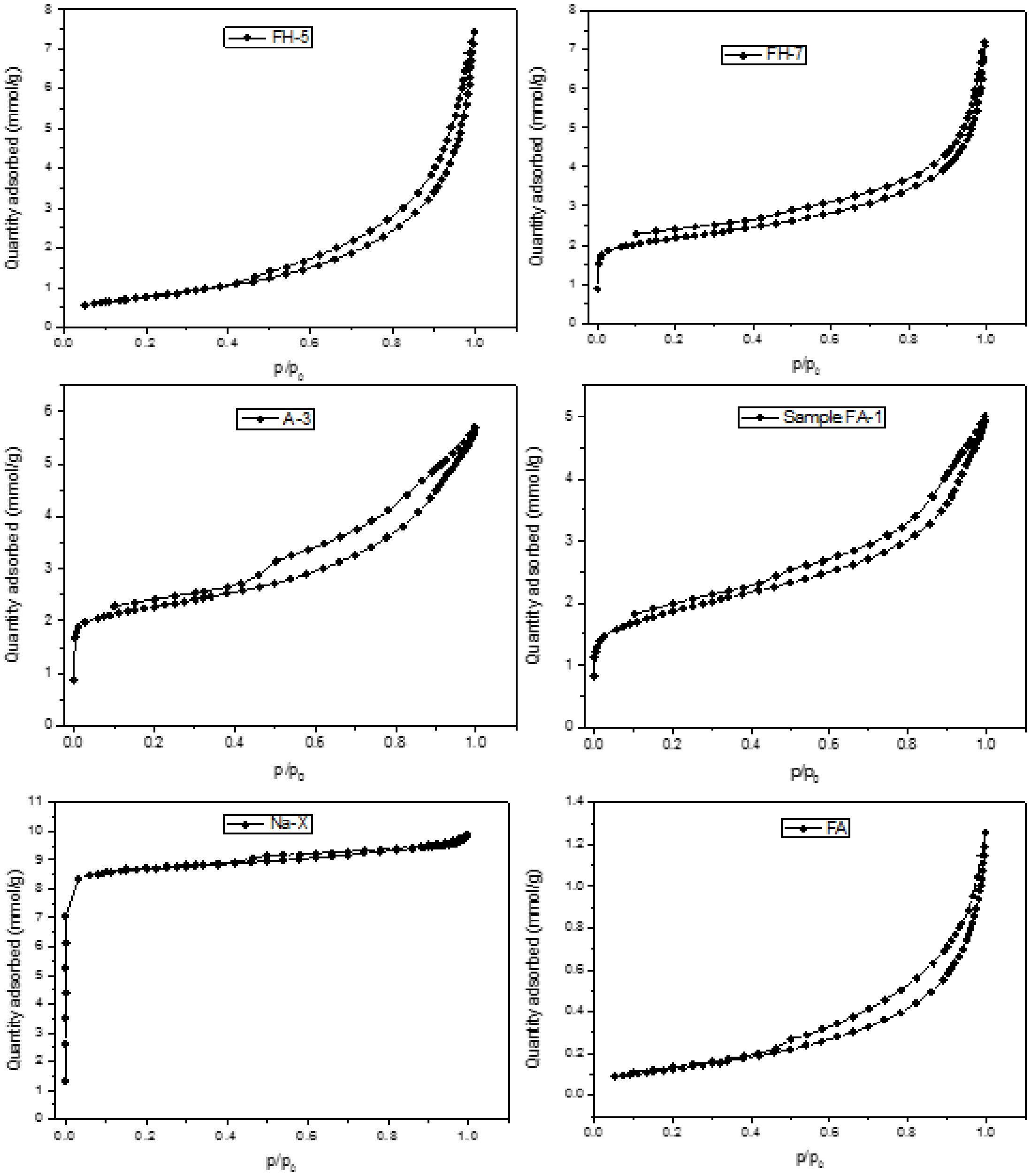

**Fig. 1.** Experimental $N_2$-adsorption/desorption isotherms of the raw fly ash, fly ash zeolites and referent Na-X.

FAZ FH-7, FAZ A-3 and FAZ FA-1 are mainly composed of Na-X phase obtained from one and the same raw material by different techniques. The all investigated Na-X fly ash zeolites exhibit isotherms very closed to type IV with hysteresis loops of H4 shape. Unlike to the pure FAU, adsorption of $N_2$ on Na-X FAZ takes part slightly in the monolayer region (less than 2 mmol/g) and much stronger at higher $p/p_0$ values. At middle $p/p_0$ range a progressive adsorption process takes part leading to capillary condensation in mesopores. Adsorption and desorption branches do not go over describing open isotherms with broad loops, which are indicative for wide pore size distribution and the presence of narrow slits. The broadest hysteresis region is observed for FAZ A-3. Sample FH-7 behaves very sharp adsorption at high pressures $p/p_0 \rightarrow 1$, which can be obeyed by macropore filling. The adsorption capacity of the pure Na-X toward $N_2$ at studied conditions reaches about 10 mmol/g, while those of FAZ varies between 5.0 and 7.5 mmol/g at $p/p_0=1$, as the highest values are reached for ash zeolites obtained by a double stage fusion-hydrothermal synthesis. FA is characterized by a negligible $N_2$ adsorption capacity around 1.3 mmol/g.

### *BET specific surface area*

The BET specific surface area ($S_{BET}$, m$^2$/g) of the investigated samples was evaluated applying the multipoint Brunauer–Emmett–Teller (BET) method to the experimental nitrogen adsorption data . Taking into account the transform contributed by Rouquerol et al. [20] for adjusting range used for fitting BET parameters at microporous materials, it was found that for the investigated FAZ, the function $1/Q[(p_0/p)-1]=f(p/p_0)$, where Q is the adsorbed volume, is linear in the range $p/p_0=0.01$-0.05, corresponding to the monolayer adsorption region, where the BET constant C takes positive values.

$S_{BET}$ values correspond to the total area, that includes the external surface of the particles and the internal surface described by pores. Typical BET plots for Na-X FAZ and the referent Na-X are presented in Fig. 2.

It is clearly seen the linearity of the adsorption functions at $p/p_0=0.01$-0.05 and the positive Y-intercept (C>0), which is indicative for the reliability of the BET calculations. Into the insertion in Fig.2, the knee of monolayer adsorption is presented.

The obtained data for $S_{BET}$ are summarized in Table 2. Fly ash has a very low BET surface area of 10 m$^2$/g, whereas FAZ zeolites possess $S_{BET}$ values from 6 to 28 times higher. FAZ of Na-X types are characterized with higher values of BET surface area than those composed of Na-A phase. The highest $S_{BET}$ is measured for FAZ A-3 due to its strongest crystallinity in comparison to the other samples. Fly ash zeolites of Na-X type have three to five times lower specific surface area in comparison to the referent FAU sample. Despite of this and taking into account the benefits of ecological effect of FA conversion into zeolites, FAZ of Na-X type obtained by different techniques are characterized with sufficient surface characteristics, which make them suitable materials for gas-adsorption purposes for removal of different atmospheric pollutants.

### *Micro- and mesopore volume/area distribution*

The internal surface area described by micropores ($S_{micro}$, m$^2$/g) and the micropore volume ($V_{micro}$, m$^3$/g) was calculated using t-plot model (Table 2). Macro- and mesopore size distribution

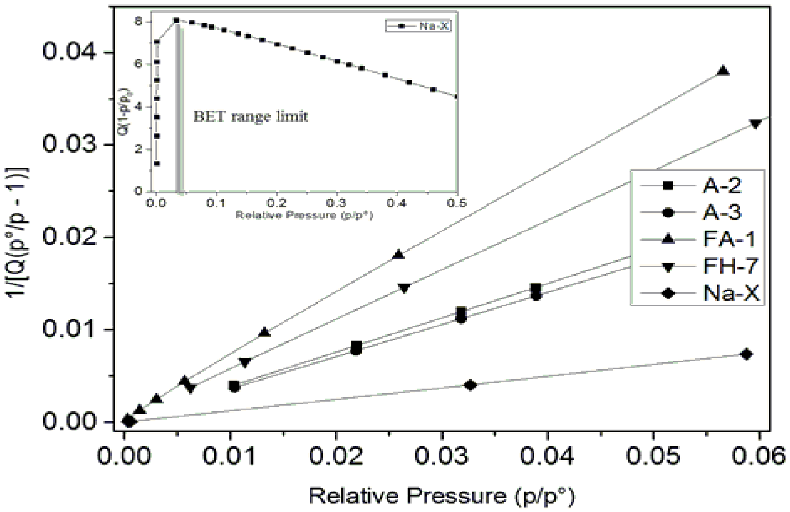

**Fig. 2.** BET plots for FAZ and referent Na-X.

**Table 2**. Surface characteristics and porosity of raw fly ash, fly ash zeolites and referent Na-X.

| Characteristics | Samples | | | | | | |
|---|---|---|---|---|---|---|---|
| | FA | A-3 | A-2 | FH-5 | FH-7 | FA-1 | Na-X |
| $S_{BET}$, $m^2/g$ | 10.4 | 279.6 | 262.4 | 60.7 | 181.7 | 146.4 | 779.8 |
| $S_{micro}$, $m^2/g$ | - | 119.4 | 173.8 | - | 109.5 | 45.5 | 718.6 |
| $V_{micro}$, $cm^3/g$ | - | 0.048 | 0.069 | - | 0.044 | 0.025 | 0.275 |
| $S_{meso/macro}$, $m^2/g$ | 13.9 | 84.6 | 78.0 | 77.2 | 83.8 | 97.0 | 62.5 |
| $V_{meso/macro}$, $cm^3/g$ | 0.012 | 0.116 | 0.105 | 0.119 | 0.103 | 0.105 | 0.055 |
| Average mesopore width, nm | 5.8 | 5.6 | 5.7 | 6.2 | 5.3 | 4.8 | 3.5 |
| Average micropore width, nm | - | 1.36 | 1.29 | - | 1.33 | 1.38 | 1.35 |

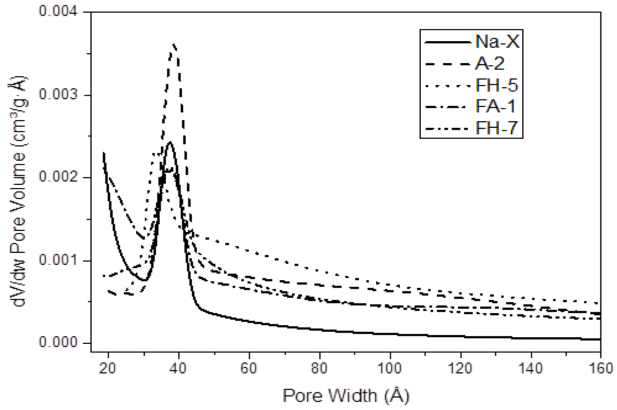

**Fig. 3.** Pore size distribution functions of investigated FAZ and the referent Na-X.

was studied by the Barrett-Joyner-Halenda (BJH) model applied to the desorption branch of the experimental isotherms. The obtained results for adsorption cumulative surface area ($S_{meso/macro}$, $m^2/g$) and cumulative volume ($V_{meso/macro}$, $cm^3/g$) of meso- and macropores with diameters between 1.7 and 300.0 nm, are listed in Table 2. The obtained values show that the referent zeolite Na-X is mostly microporous material with a small yield of meso- and macropores, while FAZ of Na-X type possess mixed micro-, meso-, and macroporous structure. Nevertheless, the samples consisting of high quantity of FAU phase obtained by atmospheric self-crystallization (A-2 and A-3) and two stage fusion-hydrothermal synthesis (FH-7) are predominantly microporous. Evidently, lack of micropores is observed at FA and FAZ of LTA type, which corresponds to their isotherms. The highest yield of meso- macroporosity is observed at the FAZ obtained by two stage fusion-atmospheric crystallization.

Pore width distribution functions in the mesoporous region of investigated FAZ and the referent Na-X are presented in Fig. 3. Average mesopore width calculated from desorption data by BJH method is given in Table 2. The mesoporosity of FAZ of FAU type and the referent zeolites is dominated by pores with sizes around 4 nm, while for FH-5 composed of LTA phase the maximum of distribution function is shifted toward 3 nm but significant amount of pores with sizes between 4-8 nm can be also observed. That is why, the highest average mesopore width is obtained at FH-5. Average micropore width calculated by BET method varies slightly and is comparable to the value for the referent Na-X.

The dependence of micropore percentage and the yield of the Na-X phase is presented in Fig. 4. The microporosity exceeds as higher is the crystallinity of the samples obtained by atmospheric self-crystallization. Sample FH-7 prepared by two stage fusion-hydrothermal synthesis is characterized with high yield of FAU zeolite comparable to that at A-3 but contains lower quantity of micropores.

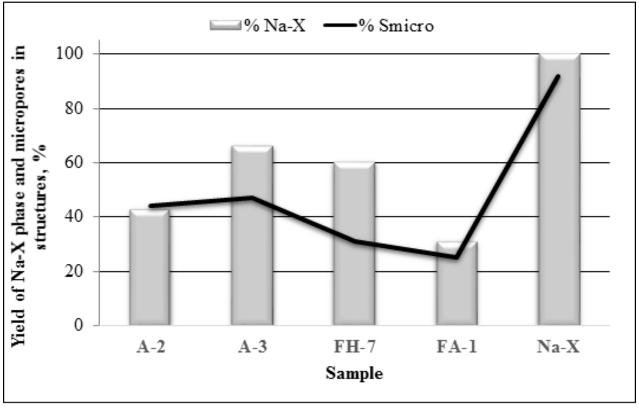

**Fig. 4.** Dependence between the yields of micropore surface area and Na-X phase.

## CONCLUSIONS

Fly ash zeolites of Na-X (Faujasite, FAU) type synthesized from coal fly ash by different techniques were studied with respect to their surface characteristics by experimental adsorption and desorption isotherms. Coal fly ash zeolites of FAU type obtained by different ways possess similar adsorption behavior which describes by isotherms of type IV with hysteresis loops corresponding to a micro-mesoporous texture. Surface parameters such as BET surface area, internal micro- and mesopore surface and volume, as well as pore size distribution were evaluated applying standard multipoint BET, BJH and t-plot models to the experimental data. The obtained results were compared with those for the raw fly ash and the referent FAU. The highest specific BET surface area of 280 $m^2/g$ was measured for coal fly ash zeolite of Na-X type, and despite that is roughly three times lower in comparison to the referent sample, it enlarges fly ash surface more than 28 times The yield of micropores in FAU based on coal ash depends on their crystallinity and the synthesis technique, whereas the yield of mesopores is dominant at all fly ash zeolites. Average mesopore width for Na-X fly ash zeolites was found in a sort range between 4.8 and 5.7 nm, as the main part of the porosity is due to pores with width about 4 nm, which is indicative for structural definiteness. It could be expected that mesoporosity of fly ash zeolites will facilitate mass transport though the materials which will be of benefit for their application for adsorption of gas molecules. Mesopore size will worse their selectivity in a case of application as molecular sieves. On the other hand, it could be expected stronger affinity toward polar $CO_2$ molecules that will decide the drawbacks of structural diversity.

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# ИЗСЛЕДВАНИЯ НА ПОВЪРХНОСТНИТЕ ХАРАКТЕРИСТИКИ НА ЗЕОЛИТИ ОТ ЛЕТЯЩА ПЕПЕЛ ЧРЕЗ ИЗОТЕРМИ НА АДСОРБЦИЯ И ДЕСОРБЦИЯ

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## (Резюме)

Зеолитите от типа Na-A (LTA) и Na-X (FAU) са перспективни адсорбенти в системи за опазване на околната среда, благодарение на изключително развитата им повърхност и размер на порите, надвишаващ молекулните диаметри на широка гама газообразни замърсители. Напоследък интензивно се синтезират аналози на тези зеолити от отпадъчни алумосиликати с цел опазване на природните ресурси. За целите на настоящето изследване са синтезирани LTA и FAU зеолити чрез алкална конверсия на летяща пепел от въглища с оглед последващото им прилагане за адсорбцията на въглероден диоксид от димни газове. Основните ключови фактори, предопределящи адсорбционната способност на твърдите вещества, са тяхната повърхност и порьозност. В тази връзка са изследвани повърхностните характеристики на избрани образци от синтезираните въглищни зеолити с помощта на порьозиметър Tristar II 3020, Micromeritics. Построени са експериментални изотерми на адсорбция и десорбция с аналитичен газ азот 5N при 77 K. Специфичната площ ($S_{BET}$, $m^2/g$) на изследваните образци е определена чрез прилагането на модела на Brunauer-Emett-Teller (BET) към данните от адсорбционните изотерми. Изходната летяща пепел се характеризира с много ниска специфична повърхност от 10 $m^2/g$, докато стойностите на $S_{BET}$ за синтезираните пепелни Na-X зеолити са в диапазона 125-250 $m^2/g$ в зависимост от условията на синтез. В рамките на настоящето изследване, най-голяма повърхност по BET от 280 $m^2/g$ е измерена за пепелен зеолит от FAU тип, получен чрез самокристализация на сместа от летяща пепел, натриева основа и вода в продължение на около година. Тези стойности са до три пъти по-ниски в сравнение с $S_{BET}$ на референтен Na-X зеолит, синтезиран от чисти изходни компоненти. Разпределението на мезопорите на материалите по размер е изчислено от данните от експерименталните десорбционни изотерми чрез прилагането на модела на Barrett-Joyner-Halenda (BJH). Обемът, площта и делът на микропори са изчислени от адсорбционните изотерми с помощта на t-plot модела.